

ably the Cu-Cu interaction. The well defined maximum at 3.9–4.0 Å in each ARDF includes trans O–O, “secondary” Cu–O, and Cu–Cl interactions. The shoulder at *ca.* 4.4 Å may be related to trans O–Cl and trans Cl–Cl interactions. The well defined peak at 5.0–5.1 Å in each ARDF is due to trans Cl–Cl as well as to tertiary Cu–Cl interactions. No other model will account for the peaks observed in the ARDF’s.

Conclusions

Cu(II), with an ionic potential between that of Co(II) and Zn(II), behaves in a fashion similar to neither with regard to the resultant complexes in concentrated aqueous solutions of the metal(II) halides. CoCl₂ dissociates completely to form Co(H₂O)₆²⁺ even in 3.6 M aqueous solutions,³⁵ whereas in the corresponding aqueous solutions of CuCl₂, solute association is the predominant solution feature. At similar concentrations ZnCl₂ neither associates nor dissociates significantly, and ZnCl₂(H₂O)₂ is the mean species in aqueous

(48) G. W. Brady and J. T. Krause, *J. Chem. Phys.*, **27**, 304 (1957); G. W. Brady, *ibid.*, **28**, 464 (1958).

(49) S. E. Lee and R. Kaplow, *Science*, **169**, 477 (1970).

(50) D. L. Wertz, *J. Soln. Chem.*, in press.

solutions of ZnCl₂.^{37,47} While Cu(II) has a greater tendency toward solute association than does the harder Zn(II) or the softer Co(II) in the concentrated metal(II) halide solutions, it is not clear whether these data indicate that Cu(II) prefers to bond to chloride to a greater extent than does Zn(II) or whether the inherent tendency of Cu(II) to achieve the tetragonally distorted octahedral ligand environment is the principal driving force in these processes. However, the basic electrostatics of the hard-soft metal-ligand interactions are contradicted by Cu(II), since, under comparable conditions, the softer Co(II) strongly prefers oxygens to chlorides and the harder Zn(II) shows no marked preference toward oxygens or chlorides.

The ligand stereochemistry about Cu(II) in these aqueous solutions is significantly similar to the wide variety of stereochemistries reported for Cu(II) in crystals. The mean Cu–O and Cu–Cl distances are 1.90–1.95 and 2.43 Å, respectively, in these solutions. Based upon our model and subsequent calculations, the Cu–Cl_{ax} distance is 2.55 Å, if it is assumed that the Cu–Cl_{eq} distance is 2.27 Å as in various chloroaquo complexes of Cu(II) in crystals.

Role of the Five-Coordinate Intermediate in the Stereochemistry of Dissociative Reactions of Octahedral Compounds

Charles S. Springer, Jr.

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790. Received July 15, 1972

Abstract: Compound topological graphs have been presented which allow the systematic analysis of the stereochemical aspects of any substitution or stereoisomerization reaction of an octahedral six-coordinate compound which proceeds *via* a five-coordinate intermediate capable of rearranging according to the Berry pseudorotation mechanism. Examples are given of a substitution reaction of a complex with monodentate ligands and intramolecular isomerization reactions of tris bidentate chelates.

Five-coordinate intermediates or transition states have often been implicated in the substitution and isomerization reactions of octahedral coordination complexes.¹ In such a case, the stereochemical aspects of the reaction are strongly related to the stereochemical fate of the five-coordinate species. The most general and economical way to depict these relationships is through the use of a compound topological graph relating the six-coordinate potential energy surface to the five-coordinate potential energy surface. This type of approach has been used very elegantly for the study of the reactions *via* five-coordinate intermediates of tetrahedral four-coordinate phosphorus² and sulfur³ com-

pounds. Qualitative mechanistic features (including the operation of the principle of microscopic reversibility) are rendered quite obvious, and even quantitative activation considerations can be facilitated.²

The General Complex Containing Monodentate Ligands. The most general six-coordinate complex is one in which all six ligands are distinguishable, M(L₁L₂L₃L₄L₅L₆). For an octahedral structure, there are 30 possible stereoisomers, and the six-coordinate surface can be visualized as a regular pentagonal dodecahedral graph where the 30 edge midpoints represent the stereoisomers.⁴ Removal of ligand number six generates the intermediate five-coordinate species M(L₁L₂L₃L₄L₅). Direct determination of the structure of such a transient species is often difficult if not impossible; so one employs the assumption that the structural propensities of this intermediate are similar to those of stable five-coordinate compounds which are overwhelmingly in favor of the trigonal bipyramid

(1) (a) R. K. Pomeroy, R. S. Gay, G. O. Evans, and W. A. G. Graham, *J. Amer. Chem. Soc.*, **94**, 272 (1972); (b) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970); (c) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 249 ff, and references cited therein. (d) F. R. Nordmeyer, *Inorg. Chem.*, **8**, 2780 (1969).

(2) K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970).

(3) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schrititz, D. J. Duchamp, and D. C. Garwood, *J. Amer. Chem. Soc.*, **92**, 7369 (1970).

(4) E. L. Muetterties, *ibid.*, **90**, 5097 (1968).

Table I. Stereoisomeric Labels

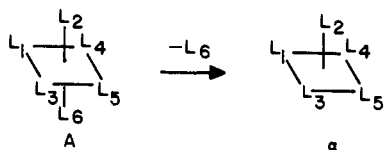
Octahedral ^a		Square pyramidal ^b		Trigonal bipyramidal ^c	
(12)(3456) \bar{F}	(12)(3654) F	(1)(2345) ξ	(1)(2543) $\bar{\xi}$	(12)(345) a	(12)(354) \bar{a}
(12)(3465) \bar{I}	(12)(3564) I	(1)(2354) ω	(1)(2453) $\bar{\omega}$	(13)(245) b	(13)(254) \bar{b}
(12)(3645) \bar{K}	(12)(3546) K	(1)(2534) δ	(1)(2435) $\bar{\delta}$	(14)(235) c	(14)(253) \bar{c}
(13)(2456) \bar{E}	(13)(2654) E	(2)(1345) μ	(2)(1543) $\bar{\mu}$	(15)(234) d	(15)(243) \bar{d}
(13)(2465) \bar{L}	(13)(2564) L	(2)(1354) $\bar{\alpha}$	(2)(1453) α	(23)(145) e	(23)(154) \bar{e}
(13)(2645) H	(13)(2546) \bar{H}	(2)(1534) λ	(2)(1435) λ	(24)(135) f	(24)(153) \bar{f}
(14)(2356) B	(14)(2653) \bar{B}	(3)(1245) β	(3)(1542) $\bar{\beta}$	(25)(134) g	(25)(143) \bar{g}
(14)(2365) \bar{M}	(14)(2563) M	(3)(1254) ν	(3)(1452) $\bar{\nu}$	(34)(125) h	(34)(152) \bar{h}
(14)(2635) \bar{G}	(14)(2536) G	(3)(1524) \bar{i}	(3)(1425) i	(35)(124) i	(35)(142) \bar{i}
(15)(2346) N	(15)(2643) \bar{N}	(4)(1235) ϵ	(4)(1532) ϵ	(45)(123) j	(45)(132) \bar{j}
(15)(2364) A	(15)(2463) \bar{A}	(4)(1253) ρ	(4)(1352) $\bar{\rho}$		
(15)(2634) \bar{J}	(15)(2436) J	(4)(1523) ϕ	(4)(1325) $\bar{\phi}$		
(16)(2345) C	(16)(2543) \bar{C}	(5)(1234) $\bar{\chi}$	(5)(1432) χ		
(16)(2354) O	(16)(2453) \bar{O}	(5)(1243) γ	(5)(1342) $\bar{\gamma}$		
(16)(2534) D	(16)(2435) \bar{D}	(5)(1423) $\bar{\kappa}$	(5)(1324) κ		

^a The first parentheses contain L_1 and the ligand trans to it in numerical order. The second parentheses contain the four ligands in the plane perpendicular to the imaginary C_4 axis containing L_1 , in clockwise order, as viewed from L_1 , starting with the lowest number. The upper case letter labels correspond to those of Gielen and coworkers (M. Gielen and C. Depasse-Delit, *Theor. Chim. Acta*, **14**, 212 (1969); M. Gielen, G. Mayence, and J. Topart, *J. Organometal. Chem.*, **18**, 1 (1969)). The stereoisomer characterized by a barred symbol is the enantiomer of the stereoisomer corresponding to the same unbarred symbol. ^b The first parentheses contain the apical ligand. The second parentheses contain the four basal ligands arranged according to the same convention as (a). They are viewed from the apical ligand. ^c These are the labels of Lauterbur and Ramirez.⁸ The same conventions as in (a) and (b) are used. The equatorial ligands are viewed from the lowest numbered apical ligand.

(TBP) and square pyramid (SP).^{5,6} For $M(L_1L_2L_3L_4L_5)$, there are 20 TBP and 30 SP stereoisomers, and the five-coordinate surface can be visualized as another regular pentagonal dodecahedron where the 20 vertices represent the TBP isomers and the 30 edge midpoints represent the SP isomers.^{4,8}

To relate the two graphs, one must define the connective pathways between them. The process of converting an octahedral six-coordinate complex to a five-coordinate compound is more straightforward than the process of increasing the coordination number of a tetrahedral four-coordinate species to five, where the problem of edge attack *vs.* facial attack arises.^{2,3} The initial phase of bond rupture and expulsion of a ligand from an octahedral complex can be viewed simply as leading to a square pyramid where the apical ligand is the one initially trans to the leaving group.^{1c,9}

For example, the expulsion of L_6 from octahedral isomer A leads directly to SP isomer α . (The labeling



convention for stereoisomers is given in Table I.) Thus the six-coordinate surface can be connected to the five-coordinate surface by connecting the octahedral isomers with their corresponding SP isomers. One can visualize a compound graph consisting of two con-

(5) E. L. Muetterties, *Rec. Chem. Progr.*, **31**, 51 (1970), and references cited therein.

(6) Holmes, *et al.*, distinguish between the square pyramid and the tetragonal pyramid, the latter having the central atom above the plane of the four basal ligands and the former having the central atom in the plane.⁷ For the purposes of this paper, these are the same and no distinction is intended here.

(7) R. R. Holmes, R. M. Deiters, and J. A. Golen, *Inorg. Chem.*, **8**, 2612 (1969).

(8) P. C. Lauterbur and F. Ramirez, *J. Amer. Chem. Soc.*, **90**, 6722 (1968).

(9) J. G. Gordon and R. H. Holm, *ibid.*, **92**, 5319 (1970).

centric dodecahedra with the edge midpoints, representing the octahedral isomers, of the smaller one (lower energy) connected to the edge midpoints, representing the SP isomers, of the larger one (higher energy). Therefore, *in this mechanism* a six-coordinate molecule enters onto the five-coordinate surface *via* a square pyramidal intermediate. The principle of microscopic reversibility makes it seem reasonable, but does not necessarily demand, that a five-coordinate molecule exit to the six-coordinate surface *via* a square pyramid.² This is implicit in our compound graph which is constructed to allow for only this possibility. The above statements purposely do not imply anything about the relative energies of the SP or TBP structures or whether either, neither, or both are transition states or intermediates along this pathway. The actual energy profile will, of course, vary according to the chemical system,^{1c} while the graph remains generally applicable for this mechanism.

The connectivities on each surface will be determined by the mechanism governing the intramolecular stereoisomerizations of the species on that surface. Although many different mechanisms for stereoisomerizations of TBP species have been proposed,¹⁰⁻¹³ the Berry pseudorotation process (BPR) is consistent with almost all mechanistic studies reported.^{5,14,15} Several recent molecular orbital calculations have indicated that the BPR transition state is somewhat lower in energy than that of the "turnstile" rotation (TR), for the simple systems calculated.^{12,15} The BPR is the only one of the mechanisms proposed in which the molecule passes

(10) E. L. Muetterties, *ibid.*, **91**, 4115 (1969).

(11) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Accounts Chem. Res.*, **4**, 288 (1971).

(12) P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971).

(13) J. I. Musher, *J. Amer. Chem. Soc.*, **94**, 5662 (1972). See also W. G. Klemperer, *ibid.*, **94**, 6940 (1972).

(14) A. Rauk, L. C. Allen, and K. Mislow, *ibid.*, **94**, 3035 (1972), and references cited therein.

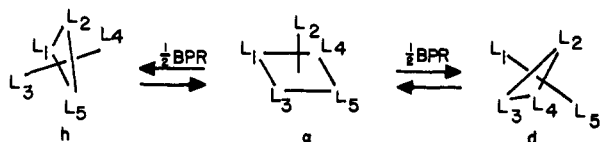
(15) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *ibid.*, **94**, 3047 (1972), and references cited therein.

through a SP structure. Thus it would seem highly reasonable that if a five-coordinate species were to isomerize after it had entered the five-coordinate surface through or near a SP structure, it would do so through a "reverse Berry"¹⁶ pseudorotation in which it would pass through or near a TBP structure.^{3,17} This is especially true if the TBP structure were lower in energy than the SP structure; a very likely possibility. Thus, although analysis of the five-coordinate surface in terms of other mechanisms¹⁸ is possible, we have chosen to consider only the BPR process in this paper.

The compound graph described above is not very useful for our purposes because, even though the dodecahedron clearly shows all SP and TBP stereoisomers, it cannot depict their relationships *via* BPR mechanisms.^{2,4,8} Muetterties has indicated that, "No three-dimensional representation can be derived ... without recourse to an interpenetrating figure."¹⁹ Two useful versions of such a figure have been derived, that of Lauterbur and Ramirez⁵ and that of Gielen and Nasielski²⁰ and Mislow and coworkers.^{2,21} The latter will be used here.

Figure 1 shows a version of Mislow's graph with the 30 edge midpoints connected to the 30 O_h stereoisomers which are shown as squares. The 30 SP isomers are shown as triangles and the 20 TBP isomers as circles. All isomers are appropriately labeled. A version with the 30 squares arranged in an inner dodecahedron proved to be too complex for easy use. The lack of connectivity of the O_h isomers expresses the tacit assumption of no intramolecular isomerization of the six-coordinate species. The compound graph has the D_{3d} symmetry of Mislow's graph (ignoring the labels). Enantiomers (g and \bar{g} , ϵ and $\bar{\epsilon}$, E and \bar{E}) are related by the center of symmetry of the graph.

With this graph, one can follow the detailed motions required by *this particular mechanism*. When a SP isomer is formed from an octahedral complex, there are two possible TBP isomers into which it can rearrange by a "reverse Berry" pseudorotation.²² There are two pairs of trans ligands in the SP structure, each of which can serve as the trans pair in a different TBP isomer. For example, isomer α (formed from A) can form either d or h by $1/2$ BPR processes. Whether either or



both are actually formed in a real system depends, of

(16) L. S. Couch and R. R. Holmes, Abstract, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972. See also R. R. Holmes, *Accounts Chem. Res.*, **5**, 296 (1972).

(17) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

(18) The word *mechanism* is used here in the same sense as that of Musher.¹³ That is, it is a description of the actual physical pathway followed by the molecule during the reaction. The BPR and TR processes are different mechanisms which belong to the same *mode* of rearrangement.¹³ They are permutationally indistinguishable^{12,13,16} because neither can produce a product unattainable by the other. For example, TBP isomer j can be converted only to TBP isomers \bar{e} , b , and \bar{a} by one-step BPR processes. One-step TR processes on j can also produce only \bar{e} , b , and \bar{a} .

(19) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969).

(20) M. Gielen and J. Nasielski, *Bull. Soc. Chim. Belg.*, **78**, 339 (1969).

(21) K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7031 (1969).

(22) This is really half of the BPR motion, and we will simply refer to it as $1/2$ BPR from now on.

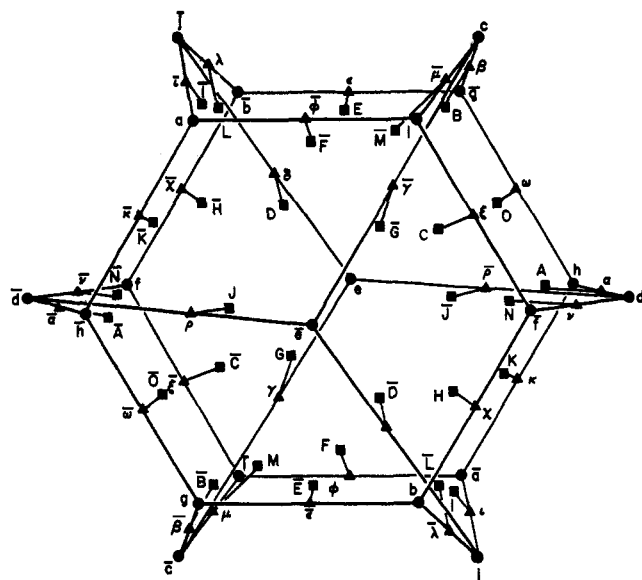
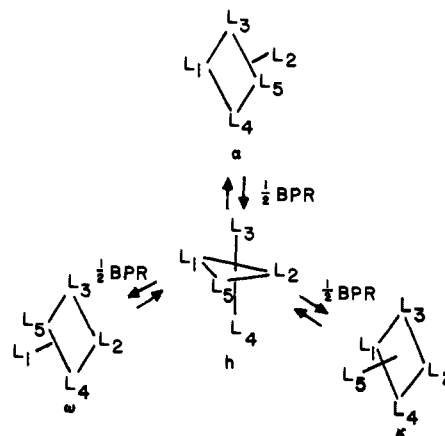


Figure 1. The compound topological graph relating the stereoisomers of the general octahedral compound $ML_1L_2L_3L_4L_5L_6$ to the stereoisomers of the general five-coordinate compound $ML_1L_2L_3L_4L_5$ specifically connected according to the Berry pseudorotation mechanism. The O_h stereoisomers are represented by squares, the square-pyramidal isomers by triangles, and the trigonal-bipyramidal isomers by circles. The labeling conventions are found in Table I.

course, on the energies involved. The two TBP isomers which can be formed from any O_h isomer by a bond rupture followed by one $1/2$ BPR motion will be identical with the two which are often given intuitively in the literature as forming directly from the O_h structure.^{10,d} Indeed the formation probably would be quite direct if the TBP structure was considerably more stable than the SP structure.

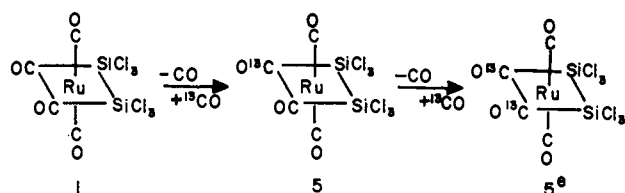
Each TBP isomer formed can go to three SP structures by $1/2$ BPR processes since there are three equatorial ligands which can serve as "pivot" ligands.⁸ For *example*, h can form ω , κ , or re-form α . These can re-



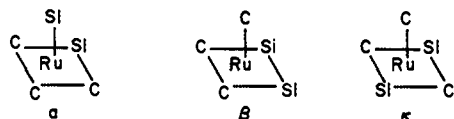
combine with the same kind of ligand as L_6 (isomerization) or a different kind of ligand (substitution) to give O_h stereoisomers O, K, and A, respectively. These are identical with the isomers which one would expect from edge attack of h .^{10,d} The minimum pathway from one O_h stereoisomer to its enantiomer, C_E ,¹⁹ involves six SP isomers and five TBP isomers (*e.g.*, $A \rightarrow [\alpha \rightarrow h \rightarrow \omega \rightarrow \bar{g} \rightarrow \epsilon \rightarrow \bar{b} \rightarrow \bar{\chi} \rightarrow f \rightarrow \bar{v} \rightarrow \bar{d} \rightarrow \bar{\alpha}] \rightarrow \bar{A}$).

An Illustrative Substitution Reaction of a Complex of

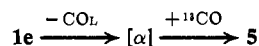
Monodentate Ligands. The graph in Figure 1 is, by nature, rather complicated. Fortunately, in most real systems, it will simplify considerably because of the reduced number of stereoisomers. As an example of the application of the general method outlined here to the reactions of octahedral complexes with monodentate ligands and how it will reduce to the intuitive result for intuitively tractable systems, let us consider the recent significant mechanistic study of Graham and co-workers.^{1a} They have carefully examined the thermal exchange of ¹³C-enriched carbon monoxide with the carbonyl ligands of Ru(CO)₄(SiCl₃)₂ at room temperature in *n*-heptane. Only the *cis* isomer (1) reacts under these conditions, and ir analyses indicate that the substitution is stereospecific to produce the mono-equatorially substituted (5) and the diequatorially substituted (5^o) products in two successive first-order steps. (The numerical labels are either those of the investigators or obvious adaptations. They are defined in the appropriate figures.)



The general compound graph can be factored down to a simpler version by converting the general isomers of Figure 1 to the stereoisomers of the problem at hand and eliminating redundant portions of the graph. Figure 2 shows an appropriate compound graph for the five-coordinate mechanism for the first step of this reaction. It should be noted that although there are only two stereoisomers of the starting compound (*cis* (1) and *trans* (2)), there are three carbonyl environments, and these must be distinguished for the leaving ligand (CO_L, C^L in Figures 2 and 3). There are only three possible TBP structures of the five-coordinate species. Muetterties has given a simplified tree version of this five-coordinate surface,¹⁰ and a compound graph of this sort would completely satisfy the requirements of this analysis. However, we have chosen to use the more complicated version in this initial treatment because the tree graph does not explicitly indicate all of the connectivities. There are only three possible SP structures corresponding to the removal of CO_L from each of its different environments.



If the SP structure formed is stereochemically rigid, the only allowed pathway for the first step is the trivial one



If the initial SP isomers formed can rearrange, there are only two possible minimum reaction pathways (remembering that that *trans* isomer does not react). These pathways can be characterized by the TBP isomers encountered, 8⁻ or 3. Pathway 8⁻ can be traversed only if the β branch to 1^a is higher in energy

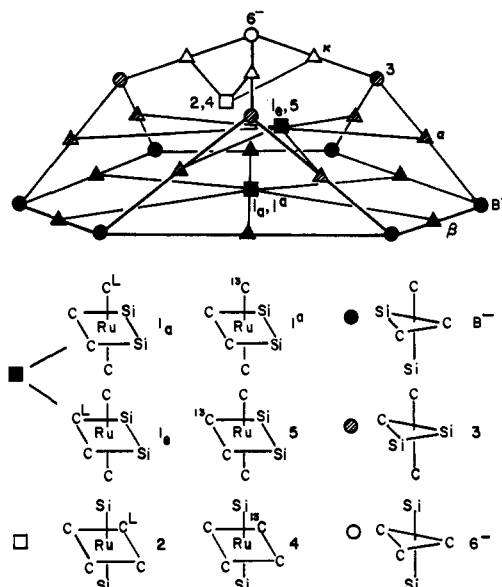
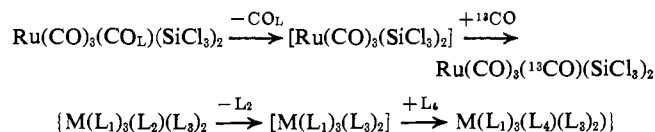
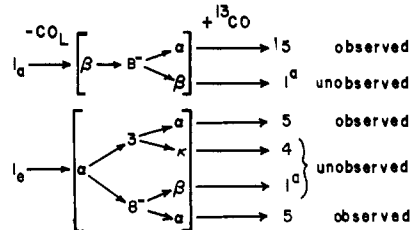


Figure 2. The compound graph for the reaction



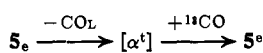
All isomers having the same energy (ignoring isotope effects) have the same symbol. The subscripts and superscripts indicate the positions of the leaving CO (CO_L, C^L) and ¹³CO, respectively. The structures of the α, β, and κ square-pyramidal isomers are given in the text. Some of the symbols are left unlabeled for simplicity; their meanings should be obvious. Many of the symbols for the octahedral isomers have been grouped together for aesthetic reasons, giving them a higher apparent connectivity than in Figure 1.



than the α branch. (None of the preceding or following statements imply that the SP structure is necessarily the high energy point of the pathway. Pathway 3 can be followed only if the κ branch to 4 is higher in energy than the α branch. The investigators clearly state that since the observed barrier for the traverse 2 → κ → 3 is prohibitively higher than the barrier for 1_e → α → 3, the principle of microscopic reversibility (PMR) demands that the barrier for 3 → κ → 4 must be higher than that for 3 → α → 5. However, the PMR does not exclude 3 → κ → 4 simply because 2 → κ → 3 is not traversed. The difference between the κ and α barriers could be enough to favor the reaction to 5 to the exclusion of that to 4. Apparently, however, this does not happen in the present case.

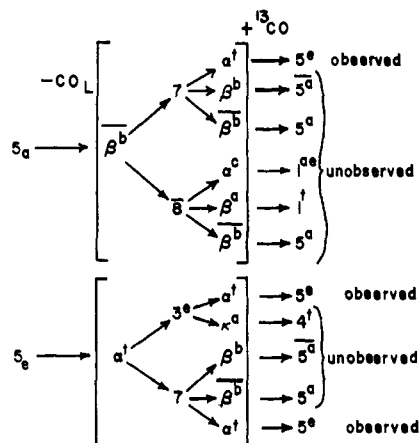
Figure 3 depicts a factored compound graph for the second step of this reaction. For this step, there are six diastereomeric CO environments, two of which are chiral (1_e^a and 5_a). There are five TBP diastereomers,

one of which is chiral (**8**). Gielen and Nasielski²⁰ and Muettterties¹⁰ have given simplified versions of this five coordinate surface. Again, the "rigid" pathway would be



Two possible minimum "nonrigid" pathways are shown in Scheme I. The enantiomeric pathways of 5^a (re-

Scheme I

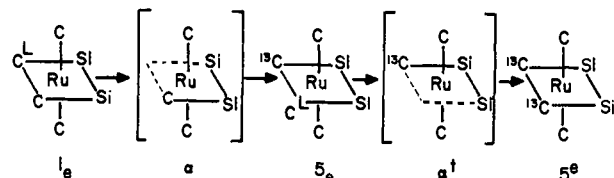


lated by the mirror planes of the graph) are also possible. From the first of these we can see that the *elimination of an axial CO can be excluded*. Since **7** should have the same energy as $\bar{8}$ and α^t the same as α^c (ignoring isotope effects), some of the unobserved 1^{ae} product would have been produced from the $\bar{8}$, α^c pathway if the observed 5^e product came from the **7**, α^t pathway. Likewise, the 8^- *axial elimination* pathway in the first step can be excluded since it has the same energy as the **7** and $\bar{8}$ *axial elimination* pathways in the second step (ignoring isotope effects).

For *equatorial CO elimination*, however, intermediate **7** (or 8^- in the first step) cannot be excluded. (We wish to thank a referee for making this clear.) If it is formed, the β barrier must be prohibitively high. Again the κ^a barrier (κ in the first step) is apparently high enough to prevent traverse.

Thus, the two simplest mechanisms which are consistent with the data for $Ru(CO)_4(SiCl_3)_2$ are the "rigid" mechanism (Scheme II) and the "nonrigid" mechanism (Scheme III).

Scheme II



In discussing the "nonrigid" mechanism, one can speculate about plausible reasons for the height of the β ($\beta^b, \bar{\beta}^b$) and κ (κ^a) barriers. Two factors which are no

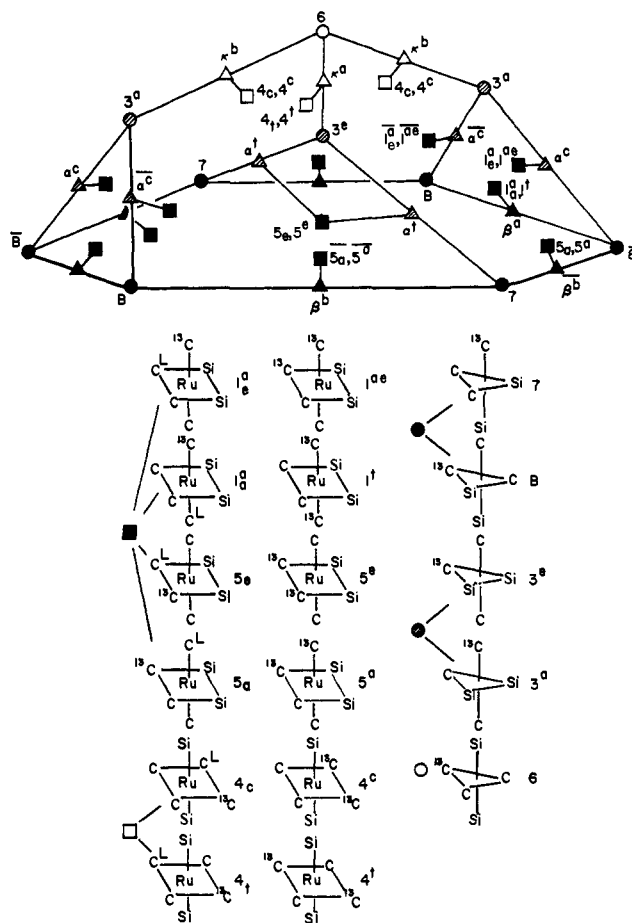
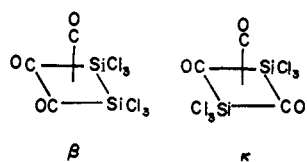
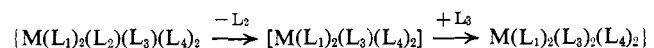
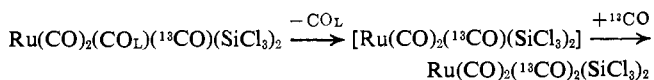


Figure 3. The compound graph for the reaction



All isomers having the same energy (ignoring isotope effects) have the same symbol. The subscripts and superscripts indicate the position of the leaving $CO(CO_L, C^L)$ and ^{13}CO , respectively. The symbols α^e and α^t , β^a and β^b , and κ^a and κ^b represent the possible monoisotopically labeled forms of α , β , and κ , respectively. As in Figure 2, some symbols are left unlabeled and some are grouped together for aesthetic reasons. Note that $\bar{8}$, the enantiomer of **8**, is different from 8^- in Figure 2.

doubt important are the relative electronegativities and π -acceptor abilities of the CO and $SiCl_3$ ligands.

The recent MO calculations of Rauk, *et al.*,¹⁴ indicate that the more electronegative substituents favor the *basal plane* in the SP structure. Thus, if the CO can be considered more electronegative than $SiCl_3$, then β and κ would be expected to be higher in energy than α where all three CO ligands are in the basal plane.

The relative π -accepting abilities of CO and $SiCl_3$ have been difficult to assess.^{1a} Hoffmann, Howell, and Muettterties have reported the preference of relatively good π acceptors for the *basal sites* in SP structures where the *central atom has no $d\pi$ electrons*.¹⁵ If this were also true for transition metal central atoms and CO were a better π acceptor than $SiCl_3$, then the β ($\beta^b, \bar{\beta}^b$) and κ (κ^a) barriers would be higher than the α (α^t) barrier. However, the latter argument is quite speculative and the π -bonding effects need further investigation.

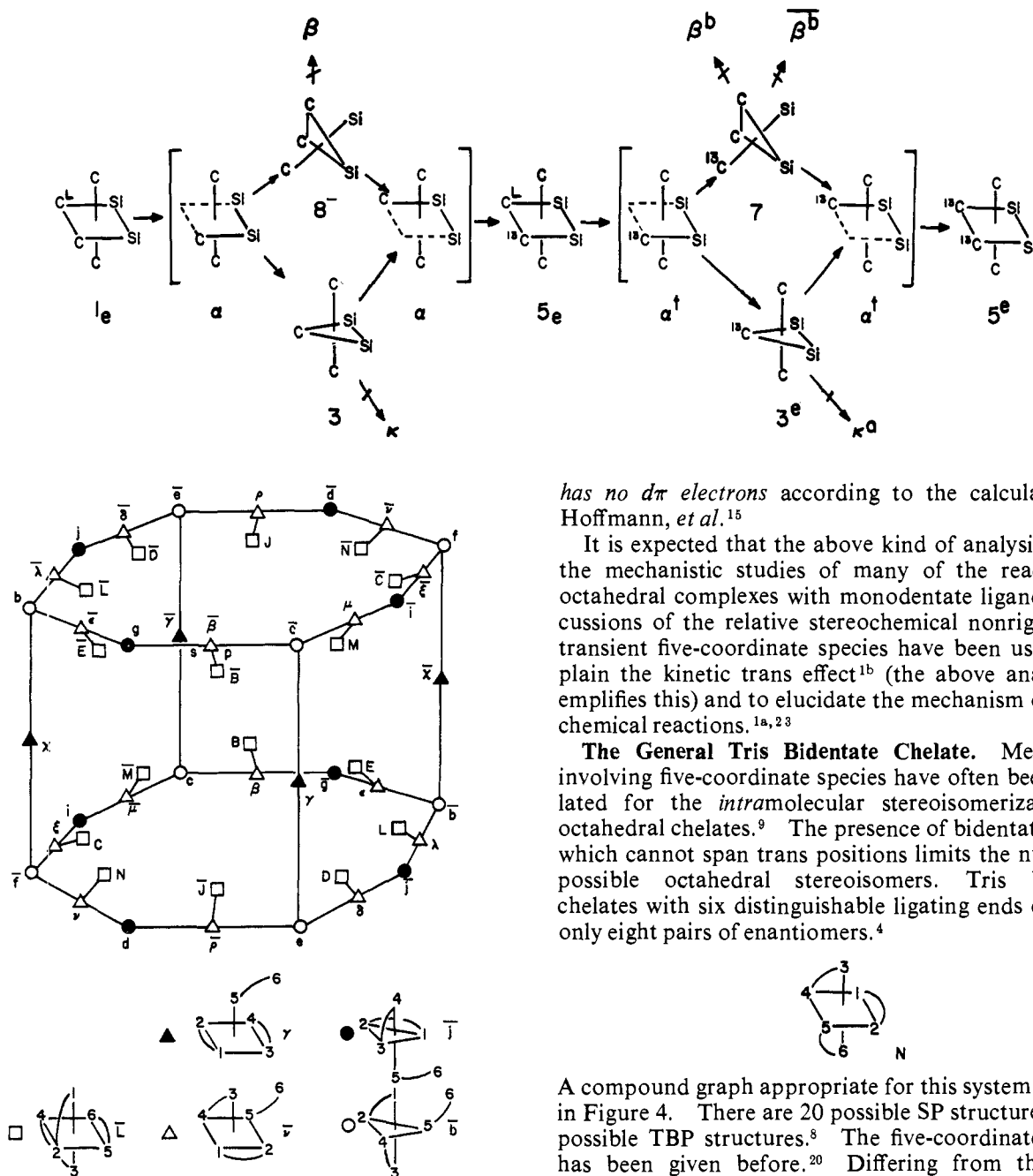
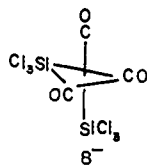


Figure 4. The compound graph for the stereoisomerization: $M(L_1L_2L_3L_4L_5L_6) \rightarrow [M(L_1L_2L_3L_4L_5)L_6] \rightarrow M(L_1L_2L_3L_4L_5L_6)$.

The TBP intermediate 8^- (7) might be expected to be higher in energy than 3 (3^e) if the above orders of relative electronegativities and π -acceptor abilities are correct. In 8^- (7), one relatively electropositive $SiCl_3$ is in

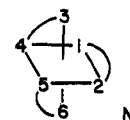


the disfavored axial position.^{14,15} This is an argument favored by Graham and coworkers.¹⁸ Also, the relatively good π -acceptor CO ligands should be in the axial positions of a TBP structure where the central atom

has no $d\pi$ electrons according to the calculations of Hoffmann, *et al.*¹⁵

It is expected that the above kind of analysis will aid the mechanistic studies of many of the reactions of octahedral complexes with monodentate ligands. Discussions of the relative stereochemical nonrigidities of transient five-coordinate species have been used to explain the kinetic trans effect^{1b} (the above analysis exemplifies this) and to elucidate the mechanism of photochemical reactions.^{1a,23}

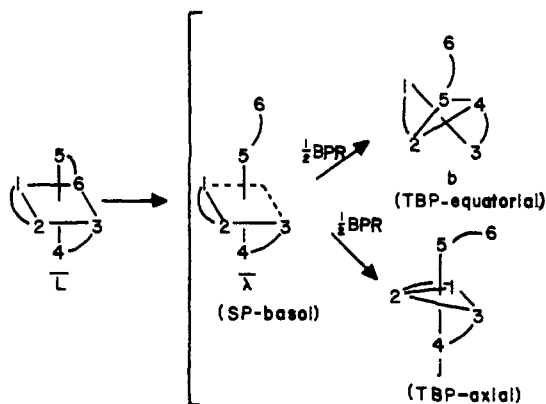
The General Tris Bidentate Chelate. Mechanisms involving five-coordinate species have often been postulated for the *intramolecular* stereoisomerizations of octahedral chelates.⁹ The presence of bidentate ligands which cannot span trans positions limits the number of possible octahedral stereoisomers. Tris bidentate chelates with six distinguishable ligating ends can form only eight pairs of enantiomers.⁴



A compound graph appropriate for this system is shown in Figure 4. There are 20 possible SP structures and 16 possible TBP structures.⁸ The five-coordinate surface has been given before.²⁰ Differing from the above monodentate systems, there are more SP isomers than there are O_h isomers. The four "extra" SP isomers (\bar{x} , \bar{y} , γ , and χ) have the monodentate ligand in the axial position. In our scheme, they cannot collapse directly to O_h structures, and consequently they are connected to TBP isomers only. These SP-axial structures isolate the two octagonal faces of the octagonal prismatic graph. The other 16 isomers have SP-basal⁹ structures. Another different feature is the existence of eight TBP isomers which are connected with only two SP isomers each (d , \bar{d} , g , \bar{g} , i , \bar{i} , j , \bar{j}). These have the monodentate ligand axial (TBP axial) and have only two possible "pivot" ligands, the two ends of the di-equatorial ligand. They connect only to isomers on one octagonal face. The TBP-equatorial isomers can act as branching points from one octagonal face to the other.

(23) C. Kutal and A. W. Adamson, *J. Amer. Chem. Soc.*, **93**, 5581 (1971).

Upon initial bond rupture of a tris bidentate chelate, an SP-basal structure is formed. This can form either a TBP-axial or a TBP-equatorial structure by $\frac{1}{2}$ BPR processes depending upon which trans pair of ligands in the



SP structure remains trans in the TBP. In a discussion considering only SP intermediates, Gordon and Holm pointed out that the SP-basal structure formed initially would have to rearrange before any isomerization could occur.⁹ Giving names to SP rearrangement processes first visualized by Fortman and Sievers,²⁴ they defined a primary process and a secondary process. Each process produced a different SP-axial isomer directly. For SP-basal isomer $\bar{\lambda}$ (formed from \bar{L}), the primary process produces χ and the secondary process produces $\tilde{\gamma}$. Careful examination of the motions in the processes defined by Gordon and Holm indicates that the initial part of the primary process is much like the $\frac{1}{2}$ BPR which produces the TBP-equatorial isomer and would take the molecule very near that structure. The initial part of the secondary process is much like the $\frac{1}{2}$ BPR which produces the TBP-axial isomer and would take the molecule very near that structure. Indeed, a glance at the graph in Figure 4 shows that χ is the first SP-axial structure encountered as the species moves from $\bar{\lambda}$ through the TBP-equatorial isomer b and that $\tilde{\gamma}$ is the first SP-axial structure encountered along the TBP-axial (j) pathway. The four O_h isomers which would be produced by Gordon and Holm's primary process from $\bar{\lambda} \rightarrow \chi$, followed by primary collapse are \bar{L} , C, \bar{E} , and N. These can be seen to be the four O_h isomers clustered about χ and isolated from the rest of the graph by TBP-axial structures. Therefore it seems more reasonable to us to consider the SP and TBP forms of the five-coordinate species together, as linked by BPR processes, than separately as has been done in the past. Accordingly we have shown the primary and secondary processes as the $\frac{1}{2}$ BPR processes producing the TBP-equatorial and TBP-axial isomers, respectively, in Figure 4.²⁵

Illustrative Stereoisomerization Reactions of Tris Bidentate Chelates. In their recent massive studies, Gordon and Holm⁹ and Girgis and Fay²⁶ have contributed a great deal toward the elucidation of the mechanism of the stereoisomerization of tris(β -diketonato)-

(24) J. J. Fortman and R. E. Sievers, *Inorg. Chem.*, **6**, 2022 (1967).

(25) The results of Gordon and Holm's secondary formation-secondary collapse process are not as easily interpreted on our graph. For example, from \bar{L} one obtains \bar{L} , C, \bar{N} , and E. Gordon and Holm do not very seriously consider this process because of the extensive amount of ligand motion involved.⁹

(26) A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, **92**, 7061 (1970).

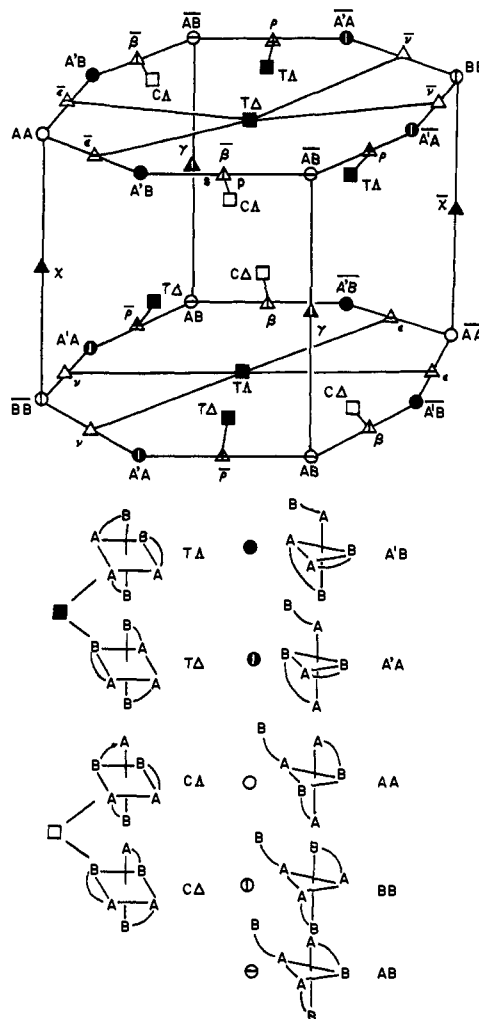
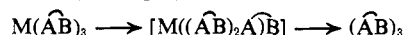


Figure 5. The compound graph for the stereoisomerization

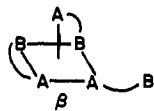


The symbolism for the TBP structures is similar to that of Muetterties,¹⁰ The square-pyramidal structures are given in the text. As in Figures 2 and 3, some of the symbols of the octahedral isomers are grouped together for aesthetic reasons.

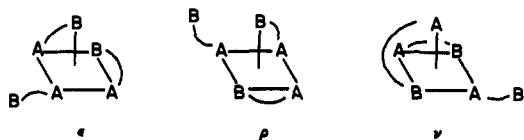
cobalt(III) complexes. They have studied tris(5-methylhexane-2,4-dionato)- and tris(benzoylacetato)cobalt(III), respectively. Their results are in quite good agreement and, although certain nonbond-rupture "twist" mechanisms cannot be ruled out completely, favor a single bond-rupture process to form an unobserved five-coordinate intermediate which collapses to give isomerization. Let us use these studies as a second and final example of the application of the general analytical scheme outlined here.

The above complexes fall into the general class of octahedral chelates with three unsymmetrical bidentate ligands, $M(AB)_3$. There are four octahedral stereoisomers for this class, *cis* Δ , *cis* Λ , *trans* Δ , and *trans* Λ and these are depicted in Figure 5, which also depicts the appropriate compound graph. There are five enantiomeric pairs for the TBP structures, four TBP-axial isomers and six TBP-equatorial isomers. A simplified version of the five-coordinate surface has been given previously.¹⁰ We have shown only the B end of the bidentate ligand as breaking free of the metal atom but, as has been noted,⁹ the stereochemical results would

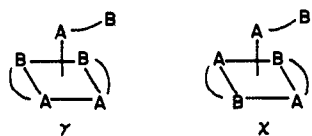
be the same if only the A ends were to break or if both ends were to break with equal probability. A cis isomer can form only one SP-basal isomer upon initial rupture because all three B ends have equivalent environments (C_3 symmetry) (e.g., $C\Delta \rightarrow \beta$).



However, a trans isomer, having no symmetry, can form three different SP-basal isomers, one for the rupture of each unique B end (e.g., $T\Delta \rightarrow \epsilon, \rho, \text{ or } \nu$).



There are two diastereomeric SP-axial isomers, γ and χ . The χ structure is chiral. Of course, these cannot collapse directly to octahedral structures.



Gordon and Holm⁹ and Girgis and Fay²⁶ find the stereoisomerizations of the cobalt chelates mentioned above to be first order and intramolecular in chlorobenzene solution. There are six microscopic rate constants for this system, and we will use the definitions given by the former authors. These are reproduced in Table II along with the relative values as measured by

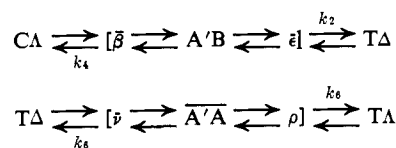
Table II. Rate Constants for Stereoisomerizations of $M(AB)_3$ Chelates

Definitions ⁹	Relative values for $\text{Co}(5\text{-methylhexane-2,4-dionate})_3$ (chlorobenzene, 90°) ⁹	Relative values for $\text{Co}(\text{benzoylacetate})_3$ (chlorobenzene, 96°) ²⁶
$C\Delta(CA) \xrightarrow{k_1} T\Delta(TA)$	11	1.1
$C\Delta(CA) \xrightarrow{k_2} TA(TA)$	100 ^a	100 ^b
$T\Delta(TA) \xrightarrow{k_3} C\Delta(CA)$	5.4	0.55
$T\Delta(TA) \xrightarrow{k_4} CA(CA)$	48	37
$C\Delta \xrightleftharpoons[k_5]{k_5} CA$	0	24
$T\Delta \xrightleftharpoons[k_6]{k_6} TA$	90	71

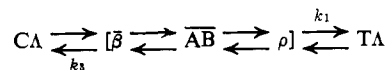
^a Absolute value = $(9.6 \pm 3.5) \times 10^{-5} \text{ sec}^{-1}$. ^b Absolute value = $(18.1 \pm 3.1) \times 10^{-5} \text{ sec}^{-1}$.

Gordon and Holm⁹ and Girgis and Fay.²⁶ A study of the numbers in this table reveals interesting results. The rate constants which are largest in both studies are k_2 , k_4 , and k_6 . Examples of shortest pathways which are amenable to these constants, according to this mech-

anism, are

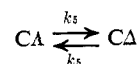


The two TBP isomers which characterize these pathways, $A'B$ and $\overline{A'A}$ (and their enantiomers which characterize the enantiomeric pathways), are the only two TBP-axial structures possible for this system. Minimum pathways which are characterized by TBP-

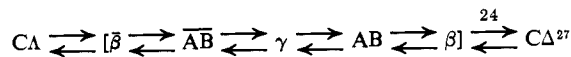


equatorial structures have smaller relative rate constants. Thus it seems that when a SP-basal isomer is formed (e.g., β from $C\Delta$), the barrier along the primary process pathway (TBP equatorial, \overline{AB}) is measurably, but not prohibitively, higher than the barrier along the secondary process pathway (TBP axial, $A'B$). The SP-basal isomer first formed upon bond rupture usually follows the secondary process pathway. Thus we have four somewhat isolated reactions on each octagonal face as the most frequent occurrences. In the case of *cis*- Δ - $\text{Co}(5\text{-methylhexane-2,4-dionate})_3$, the relative magnitudes of k_2 and k_1 indicate that the secondary process reaction occurs nine out of ten times. Gordon and Holm arrive at the same conclusion after detailed consideration of the TBP-axial and TBP-equatorial intermediates separately.

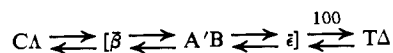
When a TBP-equatorial structure is occasionally achieved, the molecule can rearrange to a SP-axial structure and thence pass to the other octagonal face. The only observable reaction which is a direct measure of this is the enantiomerization of the cis isomers.



Gordon and Holm find this rate to be essentially unmeasurable, and thus, in their system, passage from one octagonal face to the other seems to be prohibited. This is not reflected in the studies by Girgis and Fay of $\text{Co}(\text{benzoylacetate})_3$. In their results, $k_3 > k_1$, indicating that when a TBP-equatorial isomer is formed, the barrier to the SP-axial structure is significantly lower than that to an SP-basal isomer. Comparing the relative rate of



to that of



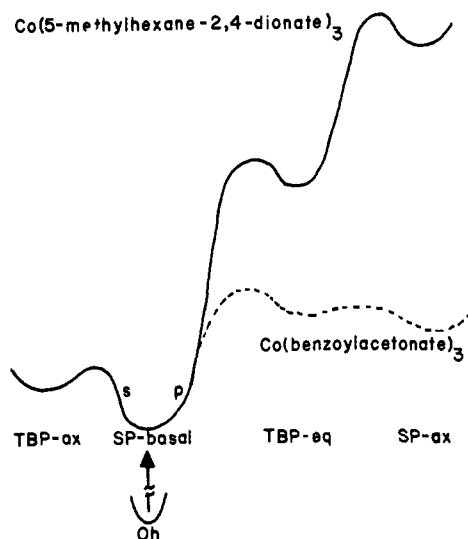
we can estimate that the primary process barrier is approximately four times as high as the secondary process barrier. Girgis and Fay reach the same conclusion considering the TBP-axial and SP-axial intermediates separately. They postulate $\sim 80\%$ TBP axial/20% SP axial.

The interpretation of these rate constants cannot be

(27) If the $\overline{AB} \rightarrow \rho$ route is not traversed to any great extent (relative rate of $C\Delta \rightarrow T\Delta$ is 1.1), then neither will be the $AB \rightarrow \beta$ route to produce $T\Delta$ from $C\Delta$ via the SP-axial intermediate, γ .

pushed too far because they were difficult to obtain and do contain significant uncertainties. However, the qualitative conclusions which could be drawn from this type of analysis might lead to the reaction profiles shown in Chart I.

Chart I



Factors which could affect the relative energies of the five-coordinate species are, as before, the relative electronegativities and π -accepting abilities of the two

different ends of the bidentate ligands and, in addition, the relative π -donating abilities and the changes in ring strain in the six-membered chelate ring in its different orientations about the central metal ion (diequatorial *vs.* apical equatorial, etc.). These are difficult to evaluate at this time.

We have investigated the kinetics of stereoisomerization of $\text{Co}(+)-3\text{-acetylcamphorate}_3$ where the chirality of the ligands causes all four octahedral stereoisomers to have different energies and allows us to make more direct measurements of the 12 microscopic rate constants than was possible in the above systems.²⁸ The results are similar to those in Table II and our analysis of their significance prompted, in part, the development of the method reported here.

The scheme described in this paper should be helpful in unifying and understanding the mechanistic results of many substitution and isomerization reactions of octahedral compounds which react *via* five-coordinate species. The same technique could be applied for other modes of five-coordinate rearrangement if it becomes apparent that processes other than the BPR are operable.

Acknowledgments. The author wishes to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Foundation of the State University of New York for support of this work.

(28) C. S. Springer, Jr., and C. Hinrichsen, unpublished results.

Stereochemically Nonrigid Eight-Coordinate Molybdenum and Tungsten Tetrahydrides

P. Meakin,* L. J. Guggenberger, W. G. Peet, E. L. Muetterties, and J. P. Jesson

Contribution No. 1956 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898. Received August 24, 1972

Abstract: Stereochemical nonrigidity has been investigated for a class of eight-coordinate transition metal hydrides. Ten hydrides of the form H_4ML_4 were prepared with L tertiary phosphines, a bidentate phosphine, and a phosphonite for molybdenum(IV) and tungsten(IV) by reaction of NaBH_4 or LiAlH_4 with L_2MCl_4 and excess L. Limiting fast- and slow-exchange nmr spectra were observed for eight of these hydrides. Rearrangement barriers are relatively high ($\Delta G^\ddagger = 12\text{--}16 \text{ kcal mol}^{-1}$), with those for the tungsten set uniformly the higher. The structure of one hydride, $\text{H}_4\text{Mo}[\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_2]_4$, was determined by single-crystal X-ray analysis. Crystals are monoclinic, space group $P2_1/c$, with cell dimensions of $a = 12.174(4) \text{ \AA}$, $b = 22.057(9) \text{ \AA}$, $c = 19.642(11) \text{ \AA}$, and $\beta = 119.68(4)^\circ$ with four molecules per cell. Structure refinement by least squares led to a conventional R of 0.071. The H_4MP_4 framework is a dodecahedron with triangular faces; the hydrogen and the phosphorus atoms are at the A and B sites, respectively (*i.e.*, vertices of elongated and flattened tetrahedra, respectively). The implications of the structural information with regard to the rearrangement process and a comparison with similar processes in HML_4 and H_2ML_4 complexes are discussed. Studies of two nine-coordinate hydrides, H_6WL_3 , are also presented.

Magnetic equivalence of ligand nuclei in eight-coordinate complexes has been a general observation.¹⁻⁶ In some instances, the magnetic equiva-

lence has been ascribed to a rapid intramolecular rearrangement, and various stylized mechanisms have been considered.¹⁻³ Preliminary nmr studies^{7,8} of eight-coordinate complexes of the type H_4ML_4 ($\text{M} =$

(1) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).
 (2) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967).
 (3) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970); *Rec. Chem. Progr.*, **31**, 51 (1970).
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(6) M. Freni, R. Demichelis, and D. Giusto, *J. Inorg. Nucl. Chem.*, **29**, 1433 (1967).
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